

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 August 2003 (21.08.2003)

PCT

(10) International Publication Number
WO 03/068177 A2

(51) International Patent Classification⁷: **A61K 7/13**

River Road, Edgewater, NJ 07020 (US). **CHAN, Alexander, Chung, Bong**; Unilever R & D Edgewater, 45 River Road, Edgewater, NJ 07020 (US).

(21) International Application Number: PCT/EP03/01400

(22) International Filing Date: 12 February 2003 (12.02.2003)

(74) Agents: **TANSLEY, Sally, Elizabeth** et al.; Unilever PLC, Patent Department, Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/075,745 14 February 2002 (14.02.2002) US

(81) Designated States (*national*): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK (utility model), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(71) Applicant (*for AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, OM, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only*): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant (*for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SN, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only*): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for IN only*): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, 400 020 Mumbai (IN).

Published:

— *without international search report and to be republished upon receipt of that report*

(72) Inventors: **SAROJINI, Padmaja**; Unilever R & D Edgewater, 45 River Road, Edgewater, NJ 07020 (US). **BARTOLONE, John, Brian**; Unilever R & D Edgewater, 45

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/068177 A2

(54) Title: TWO STEP PERMANENT COLOURING OF HAIR

(57) Abstract: A method for treating hair which comprises: first contacting said hair with a substantially inactive mixture of oxidative hair dye precursors; and allowing said mixture to remain in said hair for a period of about 30 seconds to about 60 minutes; followed by contacting said hair with a developer to achieve long lasting hair colour change, is described.

TWO STEP PERMANENT COLOURING OF HAIR

BACKGROUND OF THE INVENTION

5 The present invention relates to methods and compositions for the permanent colouring of hair which provides long lasting hair colour. The present invention also relates to methods for the colouring of hair which does not require the pre-mixing of hair colourant
10 compositions and developers just prior to application, and which can avoid the staining of hands and clothes which often occurs during conventional permanent hair colouring processes.

15 Permanent hair colour conventionally comes in two parts: a dye solution and a developer solution. In a conventional permanent hair colouring treatment, the dye solution and the developer solution are mixed and then applied to the hair, which is then left for about 25 to
20 about 45 minutes. The hair is then rinsed with water, treated with a post treatment conditioner, and then rinsed again with water.

 The application of the dye solution and the developer
25 solution affords permanent hair colouring. However, use of this conventional method does not provide maximum colour deposition or retention. In fact, in the subsequent rinse steps, a significant amount of hair colour can be washed out.

- 2 -

It would be desirable to develop methods and compositions for permanently colouring hair that maximize the amount of hair colour deposited and that minimize the amount of hair colouring that is washed out in the subsequent rinse steps.

By the methods of the present invention, durable or permanent, desired hair colour, with longer lasting hair colour change is achieved. Also in certain, permanent hair colour embodiments of the present invention, the consumer does not have to undertake any mixing step. Also the consumer may not have to use a package which mixes two discrete compositions as they are being dispensed.

Patents and patent applications related to the field of this invention are as follows:

U.S. Patent No. 5,525,123, discloses a hair dyeing composition based on oxidation dyestuff precursors which dyes and brightens the hair containing, besides at least one developer and at least one coupling agent, at least one metal salt and at least one ammonium compound selected from the group ammonium chloride, ammonium sulfate, ammonium carbonate, ammonium bicarbonate, and ammonium carbamate, having a pH-value between 8 and 11, preferably from 9 to 10, after admixture with an oxidizing agent in the ready-to-use preparation.

Co-owned and co-pending Serial No. 09/811,920 filed march 19, 2001 discloses a method for permanently dyeing hair which comprises subjecting said hair to a number of

- 3 -

treatments, having a set time interval between each two consecutive such treatments, wherein each treatment comprises steps a.) and b.) below:

- 5 a.) contacting said hair, for a period of about 5
- b.) seconds to about 5 minutes with a recently made
- mixture of:
- a.) an alkaline composition comprising a dye
- 10 intermediate in a shampoo base or in a
- conditioner base; and
- b.) an acidic composition comprising an oxidating
- compound in a shampoo base or in a conditioner
- base;
- 15 a.) rinsing said mixture from said hair with water;

with the proviso that when a conditioner base is present in a.) i.) above, an independently selected conditioner base is also present in a.) ii.) above; and when

20 a shampoo base is present in a.) i.) above, an independently selected shampoo base is also present in a.) ii.) above;

and wherein said number of treatments is between about 2 to about 30; and wherein said set time interval between

25 each two consecutive treatments is between about 8 hours and 30 days, is described.

- 4 -

SUMMARY OF THE INVENTION

The invention relates to methods and compositions for
5 achieving permanent hair colour change wherein said methods
comprise the following steps:

- 1) contacting said hair with a substantially inactive
mixture of oxidative hair dye precursors (the hair
colourant part) at a pH of about 8 or about 7 or
10 below for a period of about 30 seconds to about 60
minutes; and
- 2) contacting said hair with an oxidizing compound
(the hair colour developer part) at a pH of about
8 to about 11 for a period of about 30 seconds to
15 about 60 minutes; and
- 3) rinsing said hair with water.

DETAILED DESCRIPTION OF THE INVENTION

20

As used herein % means weight % unless otherwise
indicated. When used herein % refers to weight % as compared
to the total weight per cent of the composition that is
being discussed. For example, when % is used to discuss the
25 amount of an ingredient that is in the hair colourant part,
this means weight % as compared to the total weight of the
hair colourant part. When weight % of the hair colour
developer part is mentioned, this means the weight % as
compared to the total weight of the hair colour developer
30 part. When the ratio of the hair colourant part to the hair
colour developer part is discussed this means the ratio of

- 5 -

weight % of the hair colourant part to weight % of the hair colour developer part.

As used herein "inactive" or "substantially inactive" means that the oxidation hair dye precursors are not chemically reacting or are not chemically reacting to a substantial degree, so as to form coupled or polymerized hair colour molecules, or it means that the oxidation hair dye precursors are not chemically reacting in a substantial manner so as to form coupled or polymerized hair colour molecules.

"Hair colourant compositions of the invention" are used interchangeably with "hair colouring compositions" of the invention and "colouring compositions of the invention". "Hair colourant compositions of the invention" refers generally to those compositions of the present invention which comprise oxidative hair dye precursors. "Hair colour developer compositions of the invention" are used interchangeably with "developer compositions" of the invention. "Hair colour developer compositions of the invention" refers to those compositions of the invention which include a basifying compound that serves to activate the oxidizing agent that thereby causes the coupling, reacting or polymerization of the oxidative hair dye precursors.

As will be seen below, in some embodiments of the present invention, hair colour developer compositions comprise for example just a basifying compound and water; and others comprise a mixture of a basifying compound and a

- 6 -

peroxygen compound. As used herein the term "recently" means within a very short interval of time such as within a few seconds or minutes, such as within 0.01 seconds to 120 seconds, or within 0.1 seconds to 60 seconds, or within 0.5
5 second to within 30 seconds or within 2 seconds to within 20 seconds. Compositions of the invention may be made by means which are known in the art or which are analogous to those which are known in the art. Ingredients which are included in compositions of the invention are known in the art or may
10 be made by means which are known in the art.

The present invention relates to methods and compositions for achieving the permanent colouring of hair which methods comprise

15

- 1) contacting the hair with a substantially inactive mixture of oxidation hair dye precursors for a period of about 30 seconds to about 60 minutes, and then
- 20 2) contacting the hair with an oxidizing oxidative compound which causes said oxidation hair dye precursors to, react, couple, and polymerize so as to form large hair colour molecules within the hair shaft; and
- 25 3) rinsing said hair with water.

The first step of the above method provides hair oxidation dye precursors with time to diffuse into the hair shaft. The second step of the above method causes the
30 formation of larger sized hair colour molecules within the hair shaft. Because of their size, these larger sized hair

- 7 -

colour molecules have a very low tendency for diffusing out of the hair shaft.

The following are two non limiting embodiments of
5 methods of the present invention:

- 1) first, the substantially inactive mixture
oxidation hair dye precursors may be applied to
the hair in admixture with water and other water
10 miscible solvents at about a neutral pH and
allowed to remain on the hair for about 5 minutes
to about 60 minutes;
- 2) then a recently made mixture of an oxidizing
compound such as hydrogen peroxide, and a
15 basifying compound such as NH_4OH , which serves to
activate the oxidizing compound, is applied to the
hair for about 5 minutes to about 60 minutes;
- 3) this latter mixture of oxidizing compound and
basifying compound causes oxidation hair dye
20 precursors which have already diffused into the
hair shaft in step 1) to react, couple, and
polymerize so as to form larger hair colouring
molecules which have a low tendency to diffuse out
of the hair shaft—thus causing the formation of
25 permanent hair colour.

A second nonlimiting embodiment of a method of the
invention is as follows:

- 1) first, a substantially inactive mixture of
30 oxidative hair dye precursors and an oxidizing
agent such as hydrogen peroxide at an acidic pH,

- 8 -

may be applied to the hair and allowed to remain upon the hair for about 5 to about 60 minutes.

During this time, because said mixture is acidic, the oxidizing compound is not reactive, and the oxidation hair dye precursors do not react together, but instead diffuse into the hair shaft.

2) then a mixture of a basifying agent, such as NH_4OH is applied to the hair so as to cause the oxidizing compound to become reactive and so as to cause the oxidation hair dye precursors to react, couple, and polymerize so as to form large hair colour molecules within the hair shaft. This causes a large deposition of permanent hair colour which will not wash out.

When the first above described embodiment of methods of the invention is involved, (that is, where the basifying compound and the oxidizing compound are applied as a mixture), the compositions of the invention may be as follows:

The hair colourant compositions of the invention may comprise:

- a) about 0.001% to about 7.0% of an oxidation hair dye precursor;
- b) optionally about 0.001% to about 7.0% of a second oxidation hair dye precursor; and
- c) an aqueous carrier.

- 9 -

The hair colourant compositions of the invention may preferably comprise:

- a) about 0.01% to about 5.0% of an oxidation hair dye precursor;
- 5 b) optionally about 0.01% to about 5.0% of a second oxidation hair dye precursor; and
- c) an aqueous carrier.

10 The hair colour developer compositions of the invention may comprise

- a) about 0.1 to about 2% or about 3% or about 5% of an oxidative compound;
- b) about 0.1 to about 1.5% or about 2.0% of a basifying compound; and
- 15 c) an aqueous carrier.

The hair colour developer compositions of the invention may preferably comprise

- a) about 0.1 to about 1% of an oxidative compound;
- 20 b) about 0.1 to about 1% of a basifying agent; and
- c) an aqueous carrier.

When the second above described embodiment of methods and compositions of the invention is involved, (that is, 25 where the oxidation hair dyes are mixed in with the oxidizing compound at an acidic pH), the hair colourant compositions of the invention may be as follows:

- a) about 0.001% to about 1.0% of an oxidation hair dye precursor;
- 30 b) optionally about 0.001% to about 1.0% of a second oxidation hair dye precursor;

- 10 -

- c) about 0.1 to about 2% of an oxidizing compound;
and
- d) an aqueous carrier.

5 The hair colourant compositions of the invention may be preferably as follows:

- a) about 0.1% to about 0.8% of an oxidation hair dye precursor;
- b) optionally about 0.1% to about .8% of a second
10 oxidation hair dye precursor;
- c) about 0.1 to about 1.5% of an oxidizing compound; and
- d) an aqueous carrier.

15 In the second embodiment described above, the hair developer compositions of the invention may be preferably as follows:

- a) about 0.1 to about 1.5% of a basifying compound;
and
- 20 b) an aqueous carrier.

In the second embodiment described above, the hair developer compositions of the invention may be preferably as follows:

- 25 a) about 0.1 to about 1.0% of a basifying compound;
and
- b) an aqueous carrier.

A third embodiment of the compositions and methods of
30 the present invention would involve three steps. The first would be application of the substantially inactive mixture

- 11 -

of oxidation hair precursors for a period of about 30 seconds to about 60 minutes. The second would be an application of an acidic mixture of an oxidizing compound such as hydrogen peroxide, and the third step would be an application of a basifying compound for a period of about 5 minutes to about 60 minutes followed by rinsing.

The compositions and methods of the present invention may be used to colour different types of hair such as Asian hair and Caucasian hair.

It will be understood by those skilled in the art that concentrations of oxidative hair dye precursors which may be employed in the present invention can be varied depending on, for example, the hair type which is to be coloured and on the colouring effect which is desired.

What follows is a description of the ingredients that can be included in the compositions of the present invention.

OXIDATIVE HAIR DYE PRECURSORS

The hair colourant compositions of the present invention can include one or more oxidative hair colouring precursors, agents or dyes. Such oxidative hair colouring agents are used in combination with the oxidizing systems of the present invention to deliver permanent hair dye to the hair.

- 12 -

Permanent hair dye compositions as defined herein are compositions, which once applied to the hair, are substantially resistant to washout.

5 The dye forming intermediates used in oxidative dyes can be aromatic diamines, naphthols, aminophenols and their derivatives. These dye forming intermediates can be classified as; primary and secondary intermediates, couplers and modifiers. As used herein the term "precursor" means
10 precursor, coupler, modifier, and intermediate and the like. Primary intermediates are chemical compounds, which by themselves will form a dye upon oxidation. The secondary intermediates, also known as colour modifiers or couplers, are used with other intermediates for specific colour
15 effects or to stabilize the colour.

 The oxidation dye intermediates, which are suitable for, use in the compositions and processes herein include aromatic diamines, naphthols, polyhydric phenols,
20 aminophenols and derivatives of these aromatic compounds (e.g., N-substituted derivatives of the amines, and ethers of the phenols).

 Primary oxidation dye intermediates are generally
25 colourless molecules prior to oxidation. The oxidation dye colour is generated when the primary intermediate is 'activated' and subsequently joined with a secondary intermediate (coupling agent), which is also generally colourless, to form a coloured, conjugated molecule. In
30 general terms, oxidation hair dye precursors or intermediates include those monomeric materials which, on

- 13 -

oxidation, form oligomers or polymers having extended conjugated systems of electrons in their molecular structure.

5 Because of the new electronic structure, the resultant oligomers and polymers exhibit a shift in their electronic spectra to the visible range and appear coloured. For example, oxidation dye precursors capable of forming coloured polymers include materials such as p-
10 phenylenediamine, which has two functional groups, are capable of oxidative polymerization to yield higher molecular weight coloured materials having extended conjugated electron systems.

15 Colour modifiers (couplers), such as those detailed hereinafter, are preferably used in conjunction with the oxidation dye precursors herein and are thought to interpose themselves in the coloured polymers during their formation and to cause shifts in the electronic absorption spectra
20 thereof, thereby resulting in slight colour changes. A representative list of oxidation dye precursors suitable for use herein is found in Sagarin, "Cosmetic Science and Technology", "Interscience, Special Edition, Volume 2, pages 308 to 310 which is herein incorporated by reference.

25

 It is to be understood that the oxidizing aids of the present invention are suitable for use (in combination with a source of peroxide as detailed herein) with all manner of oxidation dye precursors and colour modifiers and that the
30 precursors detailed below are only by way of example and are not intended to limit the compositions and processes herein.

- 14 -

The typical aromatic diamines, polyhydric phenols, aminophenols, and derivatives thereof, described above as primary dye precursors can also have additional substituents on the aromatic ring, e.g. halogen, alkyl, alkyl substituted additional substituents on the amino nitrogen and on the phenolic oxygen, e.g. substituted and unsubstituted alkyl and aryl groups.

The hair colouring compositions of the present invention may, in addition to the essential oxidative hair-colouring agents, optionally include non-oxidative and other dye materials. Optional non-oxidative and other dyes suitable for use in the hair colouring compositions and processes according to the present invention include semi-permanent, temporary and other dyes. Non-oxidative dyes as defined herein include the so-called `direct action dyes`, metallic dyes, metal chelate dyes, fiber reactive dyes and other synthetic and natural Chemical and Physical Behaviour of Human Hair` 3rd Edn. by Clarence Robbins (pp 250-259); `The Chemistry and Manufacture of Cosmetics`. Volume IV. 2nd Edn. Maisson G. De dyes. Various types of non-oxidative dyes are detailed in: `Navarre at chapter 45 by G. S. Kass (pp 841-920); `cosmetics: Science and Technology` 2nd Edn, Vol. II Balsam Sagarin, Chapter 23 by F. E. Wall (pp 279-343); `The Science of Hair Care` edited by C. Zviak, Chapter 7 (pp 235-261) and `Hair Dyes`, J. C. Johnson, Noyes Data Corp., Park Ridge, U. S.A. (1973), (pp 3-91 and 113-139).

Specific hair dyes which may be included in the compositions of the invention include m-aminophenol; 3-

- 15 -

methyl-p-aminophenol; 2,3-dimethyl-p-aminophenol; p-phenylene diamine, p-toluenediamine; 2-chloro-p-phenylenediamine; N-phenyl-p-phenylenediamine; N-2-methoxyethyl-p-phenylenediamine; N,N-bis-(hydroxyethyl)-p-phenylenediamine; 2-hydroxymethyl-p-phenylenediamine; 2-hydroxyethyl-p-phenylenediamine; 4, 4'-diaminodiphenylamine; 2,6-dimethyl-p-phenylenediamine; 2-isopropyl-p-phenylenediamine; N-(2-hydroxypropyl)-p-phenylenediamine; 2-propyl-p-phenylenediamine; 1,3-p-N, N-bis-(2-hydroxyethyl)-aminoanilino- 2-propanol; 2-methyl-4-dimethylaminoaniline; p-aminophenol; p-methylaminophenol; 3-methyl-p-aminophenol; 2-hydroxymethyl-p-aminophenol; 2-methyl-p-aminophenol; 2-(2-hydroxyethylaminomethyl)-p-aminophenol; 2-methoxymethyl-p-aminophenol; and 5-aminosalicylic acid; catechol; pyrogallol; o-aminophenol; 2, 4-diaminophenol; 2,4,5-trihydroxytoluene; 1,2,4-trihydroxybenzene; 2-ethylamino-p-cresol; 2,3-dihydroxynaphthalene; 5-methyl-o-aminophenol; 6-methyl-o-aminophenol; and 2-amino-5-acetaminophenol; 2-methyl-1- naphthol; 1-acetoxy-2-methylnaphthalene; 1,7-dihydroxynaphthalene; resorcinol; 4-chlororesorcinol; 1-naphthol; 1,5-dihydroxynaphthalene; 2,7-dihydroxynaphthalene; 2-methylresorcinol; 1-hydroxy-6-aminonaphthalene- 3-sulfonic acid; thymol (2-isopropyl-5-methylphenol); 1,5-dihydroxy-1,2, 3,4-tetrahydronaphthalene; 2-chlororesorcinol; 2,3-dihydroxy-1,4- naphthoquinone; and 1-naphthol-4-sulfonic acid; m-phenylenediamine; 2-(2,4-diaminophenoxy)ethanol; N,N-bis(hydroxyethyl)-m-phenylenediamine; 2,6- diaminotoluene; N,N-bis(hydroxyethyl)-2,4-diaminophenetole; bis(2,4-diaminophenoxy)-1,3-propane; 1-hydroxyethyl-2,4-diaminobenzene; 2-amino- 4 hydroxyethylaminoanisole;

- 16 -

aminoethoxy-2,4-diaminobenzene; 2,4- diaminophenoxyacetic acid; 4,6-bis(hydroxyethoxy)-m-phenylenediamine; 2,4-diamino-5-methylphenetole; 2,4-diamino-5-hydroxyethoxytoluene; 2,4- dimethoxy 1,3-diaminobenzene; and
5 2,6-bis(hydroxyethylamino) toluene; m-aminophenol; 2-hydroxy-4- carbamoylmethylaminotoluene; m-carbamoylmethylaminophenol; 6- hydroxybenzomorpholine; 2-hydroxy-4-aminotoluene; 2-hydroxy-4-hydroxyethylaminotoluene; 4,6-dichloro-m-aminophenol; 2-
10 methyl-m- aminophenol; 2-chloro-6-methyl-m-aminophenol; 2-hydroxyethoxy-5- aminophenol; 2-chloro-5-trifluoroethylaminophenol; 4-chloro-6-methyl-m-aminophenol; N-cyclopentyl-3-aminophenol; N-hydroxyethyl-4-methoxy-2-methyl-m-aminophenol and 5-amino-4-methoxy-2-methylphenol;
15 2-dimethylamino-5-aminopyridine; -tetra-aminopyrimidine; 4,5-diamino-1-methylpyrazole; 4,5-diamino-1-hydroxyethyl pyrazole, 4,5-diamino-1-hydroxyethyl pyrazole, 1-phenyl-3-methyl-5-pyrazolone; 6-methoxy-8-aminoquinoline; 2,6-dihydroxy-4-methylpyridine; 5-hydroxy-1,4-benzodioxane; 3,4-
20 methylenedioxyphenol; 4-hydroxyethylamino-1,2-methylenedioxybenzene; 2,6-dihydroxy-3,4-dimethylpyridine; 5-chloro-2,3-dihydroxypyridine; 3,5-diamino-2,6- dimethoxypyridine; 2-hydroxyethylamino-6-methoxy-3-aminopyridine; 3,4- methylenedioxyaniline; 2,6-bis-hydroxyethoxy-3,5-diaminopyridine; 3-amino-5-hydroxy-
25 2,6-dimethoxypyridine; 5,6-dihydroxyindole; 7-hydroxyindole; 5-hydroxyindole; 4-hydroxyindole; 2-bromo-4,5-methylenedioxyphenol; 6-hydroxyindole; 3-amino-2-methylamino-6-methoxypyridine; 2-amino-3-hydroxypyridine; 2,6-diaminopyridine; 5-(3,5-diamino-2-pyridyloxy)-1,3-dihydroxypentane; 3-(3,5-diamino-2-pyridyloxy)-2-

- 17 -

hydroxypropanol and 4-hydroxy-2,5,6-triaminopyrimidine, or combinations thereof.

5 SOLVENTS

Water is the preferred principal solvent, carrier or diluent for the compositions according to the present invention. As such, the compositions according to the present invention may include one or more solvents as additional solvent, carrier or diluent materials. Generally, the solvent is selected to be miscible with water and innocuous to the skin. Solvents suitable for use herein include C₁-C₂₀ mono- or polyhydric alcohols and their ethers, glycerine, with monohydric and dihydric alcohols and their ethers are preferred. In these compounds, alcoholic residues containing 2 to 10 carbon atoms are preferred. Thus, a particularly preferred group includes ethanol, isopropanol, n-propanol, butanol, propylene glycol, ethylene glycol monoethyl ether, and mixtures thereof.

These solvents may be present in the hair colourant compositions of the present invention. These solvents may be present in the hair colour developer compositions of the present invention.

- 18 -

BUFFERING AGENTS

The hair colourant compositions and the hair developer
5 compositions of the present invention may have widely
ranging pH's. When basifying agents are present in
compositions of the invention, the pH can range from about
7.0 to about 11.0. Acidic pH ranges of about 2.0 to about
4.0 may be employed in those embodiments of the present
10 invention wherein oxidation hair precursors are applied to
the hair in admixture with oxidizing compounds such as
hydrogen peroxide. This is done because such low pH's will
stabilize the hydrogen peroxide present.

15 The hair colour developer compositions of the invention
may have a preferred pH in the range of from about 7.0 or
8.0 to about 11, more preferably from about 8.0 to about
10.0.

20 Buffering agents may be present in the hair colourant
compositions of the present invention and in the hair colour
developer compositions of the invention in order to maintain
a desired pH level. The hair colourant compositions and the
hair colour developer compositions of the present invention
25 may also contain one or more hair swelling agents (HSAs)
such as urea, to adjust the pH to the desired level.

Several different pH modifiers can be used to adjust
the pH of hair colourant compositions of the present
30 invention and to adjust the pH of the hair colour developer
compositions of the present invention. Nonlimiting

- 19 -

examples of suitable buffering agents are ammonium hydroxide, urea, ethylamine, dipropylamine, triethylamine and alkanediamines such as 1,3-diaminopropane, anhydrous alkaline alkanolamines such as, mono or di- or tri-
5 ethanolamine, preferably those which are completely substituted on the amine group such as dimethylaminoethanol, polyalkylene polyamines such as diethylenetriamine or a heterocyclic amine such as morpholine as well as the hydroxides of alkali metals, such as sodium and potassium
10 hydroxide, hydroxides of alkali earth metals, such as magnesium and calcium hydroxide, basic amino acids such as L-arginine, lysine, oxylysine and histidine and alkanolamines such as dimethylaminoethanol and aminoalkylpropanediol and mixtures thereof. Also suitable
15 for use herein are compounds that form HCO_3^- by dissociation in water (hereinafter referred to as "ion forming compounds"). Nonlimiting examples of suitable ion forming compounds are Na_2CO_3 , NaHCO_3 , K_2CO_3 , $(\text{NH}_4)_2\text{CO}_3$, NH_4HCO_3 , CaCO_3 and $\text{Ca}(\text{HCO}_3)_2$ and mixtures thereof.

20

As herein before described, certain alkaline buffering agents such as ammonium hydroxide and monoethylamine (MEA), urea and the like, can also act as hair swelling agents (HSA's).

25

Preferred for use as buffering agents for the hair colourant compositions and the hair colour developer compositions according to the present invention, which are alkaline, is ammonium hydroxide and/or sodium hydroxide.

30

- 20 -

OXIDIZING COMPOUNDS

The oxidizing compounds or agents useful in the methods and compositions of the present invention are generally

5 inorganic peroxygen materials capable of yielding peroxide in an aqueous solution. Inorganic peroxygen oxidizing agents are well known in the art and include hydrogen peroxide, inorganic alkali metal peroxides such as sodium periodate, sodium perbromate and sodium peroxide, and inorganic

10 perhydrate salt oxidizing compounds, such as the alkali metal salts of perborates, percarbonates, perphosphates, persilicates, persulphates and the like. These inorganic perhydrate salts may be incorporated as monohydrates, tetrahydrates etc. Also useful are melamine peroxide, sodium

15 perborate, and sodium percarbonate. Mixtures of two or more of such inorganic peroxygen oxidizing agents can be used. For all of these compounds, the active material is active hydrogen peroxide. One skilled in the art would recognize how much active hydrogen peroxide is desired in the hair

20 colouring compositions that are being formulated and therefore one skilled in the art would be able to calculate how much of a peroxygen compound, such as for example, melamine peroxide, to employ.

25

BASIFYING COMPOUNDS

Basifying compounds may be contained in one or both of the hair colourant compositions and the hair colour

30 developer compositions of the invention. Basifying compounds may include, for example, NH_4OH .

- 21 -

In hair colouring kits of the invention which contain the hair colourant compositions of the present invention and the hair colour developer compositions of the present invention, a portion of peroxide oxidizing agent, may be present in either solid or liquid form, such as hydrogen peroxide, and an acid buffering agent solution as mentioned above may be required to stabilize the hydrogen peroxide. Since hydrogen peroxide is stable in the pH range from 2 to 4, it may be necessary to use a buffering agent having a pH within this range. Dilute acids are suitable as hydrogen peroxide buffering agents. Phosphoric acid is a preferred agent for buffering hydrogen peroxide solutions.

This pH adjustment can be also effected by using well known acidifying agents in the field of treating keratinous fibers, and in particular human hair, such as inorganic and organic acids such as hydrochloric acid, tartaric acid, citric acid, and carboxylic or sulphonic acids such as ascorbic acid, acetic acid, lactic acid, sulphuric acid, formic acid, ammonium sulphate and sodium dihydrogenphosphate/phosphoric acid, disodium hydrogen phosphate/phosphoric acid, potassium chloride/hydrochloric acid, potassium dihydrogen phthalate/hydrochloric acid, sodium citrate/hydrochloric acid, potassium dihydrogen citrate/hydrochloric acid, potassium dihydrogencitrate/citric acid, sodium citrate/citric acid, sodium tartarate/tartaric acid, sodium lactate/lactic acid, sodium acetate/acetic acid, disodium hydrogenphosphate/citric acid and sodium chloride/glycine/hydrochloric acid and mixtures thereof.

- 22 -

THICKENERS

Thickeners may be optionally included in the oxidation hair colourant compositions and hair developer compositions of the invention, and specifically thickeners may be included in the hair colourant part and the hair colour developer parts of the invention. Long chain fatty alcohols having from about 11 to about 18 carbon atoms in the long fatty chain can be thickener constituents of the compositions of this invention. These alcohols can be used alone, or in admixture with each other. When included in the compositions, the alcohol is preferably present at from about 0.5 to about 10 weight percent of the composition, and more preferably at from about 2 to about 5 weight percent.

15

Lauryl alcohol, oleyl alcohol, myristyl alcohol, stearyl alcohol, and the like, and mixtures thereof are contemplated herein as thickeners. In addition, mixtures of natural or synthetic fatty alcohols having fatty chain lengths of from about 11 to about 18 carbons are also useful. Several such mixtures are available commercially, and are exemplified by the material containing a mixture of synthetic alcohols with 12 to 15 carbons in the alkyl chain sold under the trademark NEODOL 25 by Shell Chemical Company, and the material containing a mixture of synthetic alcohols with chain lengths of 12 to 16 carbons sold under the trademark ALFOL 1216 Alcohol by Conoco Chemicals.

Thickening agents suitable for use in the compositions herein may also be selected from oleic acid, cetyl alcohol, oleyl alcohol, sodium chloride, cetearyl alcohol, stearyl

30

- 23 -

alcohol, synthetic thickeners such as Carbopol, ACULYN, STRUCTURE, and Acrosyl and mixtures thereof. Preferred thickeners for use herein are Aculyn 22 (RTM), steareth-20 methacrylate copolymer; Aculyn 44 (RTM) polyurethane resin
5 and Acusol 830 (RTM), acrylates copolymer that are available from Rohm and Haas, Philadelphia, Pa., USA. Additional thickening agents suitable for use herein include sodium alginate or gum arabic, or cellulose derivatives, such as methyl cellulose or the sodium salt of
10 carboxymethylcellulose or acrylic polymers.

Fatty alcohols of the above discussed carbon chain lengths which are ethoxylated to contain an average of one or two moles of ethylene oxide per mole of fatty alcohol can
15 be used in place of the fatty alcohols themselves. Examples of such useful ethoxylated fatty acids include ethylene glycol cetyl ether, polyoxyethylene (2) stearyl ether, and the like; the exemplary compounds having CTFA Dictionary names of Ceteth-1 and Steareth-2, respectively.

20

OTHER OPTIONAL INGREDIENTS

The hair colourant compositions and hair developer
25 compositions of the invention, of the present invention can comprise a wide range of optional ingredients. Examples of these functional classes include: anticaking agents, antioxidants, binders, biological additives, bulking agents, chelating agents, chemical additives, colourants, cosmetic
30 astringents, cosmetic biocides, denaturants, drug astringents, emulsifiers, film formers, fragrance

- 24 -

components, humectants, opacifying agents, plasticizers, preservatives, propellants, reducing agents, solvents, foam boosters, hydrotropes, solubilizing agents, suspending agents (nonsurfactant), sunscreen agents, ultraviolet light
5 absorbers, and viscosity increasing agents (aqueous and nonaqueous). Examples of other functional classes of materials useful herein that are well known to one of ordinary skill in the art include solubilizing agents, sequestrants, amino acids, hydrolysed proteins and the like.

10

Other optional ingredients include organic acids. A non-exclusive list of examples of organic acids which can be used as the proton donating agent is adipic acid, tartaric acid, citric acid, maleic acid, malic acid, succinic acid,
15 glycolic acid, glutaric acid, benzoic acid, malonic acid, salicylic acid, gluconic acid, polyacrylic acid, their salts, and mixtures thereof. A non-exclusive list of examples of mineral acid for use herein is hydrochloric, phosphoric, sulfuric and mixtures thereof.

20

APPLICATION OF METHODS AND COMPOSITIONS OF THE INVENTION

The hair colourant part and the hair colour developer
25 part of the present invention are applied to hair separately. By this it is meant that after the hair colourant part is contacted with the hair, a period of about 30 seconds to about 60 minutes is allowed to elapse before the hair colour developer part is contacted with the hair.
30 This is in sharp contrast to conventional permanent hair colouring methods which require that the hair be contacted

- 25 -

with a hair colourant composition and a hair colour developer composition, simultaneously or nearly simultaneously. Without being bound by theory, it is believed that an advantage of the methods of the present invention is that smaller hair dye precursor molecules are given time to diffuse into the hair shaft. Then when the hair is contacted with the hair colour developer part, the smaller hair dye precursor molecules that are within the hair shaft undergo coupling and polymerization reactions so as to form larger colour molecules that are trapped within the hair shaft because of their size. Another advantage of the methods of the present invention as compared to conventional permanent hair colouring methods, is that conventional permanent hair colouring methods cause much of the coupling and polymerization of the hair dye precursors to occur outside of the interior of the hair shaft and are wasted. Large hair colour molecules are formed, and because of their size, these large hair colour molecules cannot diffuse into the hair shaft.

20

The above physical phenomena can be described by the following chemical equations:

when rate of oxidation of hair dye precursors/ rate of diffusion of hair dye precursors ≥ 1 ,

25

Diffusion of hair colour precursor is limited by the rapid formation of dye molecules outside the hair fiber when:

30

when rate of oxidation/ rate of diffusion < 1 ,

- 26 -

* ΔE is difference of colour with undyed hair :
 $\sqrt{(\Delta L^2 + \Delta a^2 + \Delta b^2)}$

5 Assessment of Initial Colour and Colour Change

The equipment used to measure both the initial colour and colour change on substrates (hair /skin) dyed with the singly packaged low pH colouring compositions of the present invention is a Hunter Colourquest spectrophotometer. The value used to express the degree of colour change on any particular substrate is delta E (ΔE). Delta E, as defined herein, is represented by a factual sum of L, a, and b values such that:

15

ΔE = is difference of colour with undyed hair :
 $\sqrt{(\Delta L^2 + \Delta a^2 + \Delta b^2)}$

and L is a measure of lightness and darkness (colour intensity), wherein L=100 is equivalent to white, and L=0 is equivalent to black. Further, 'a' is a measure of the red and green quotients (colour hues) such that positive equates to red and negative equates to green, and 'b'. is a measure of the yellow and blue quotients (colour hues) such that positive equates to yellow and negative equates to blue.

The following examples below, which were made, are shown as illustrations only and are not intended to limit the scope of the invention.

30

The examples just below show that the two step process of the present invention results in longer lasting hair

- 27 -

colour change that is more resistant to methanol extraction,
for example. The compositions, which are used just below,
were prepared for these laboratory tests and do not include
ingredients such as for example fragrances, which would
5 ordinarily be employed in commercial compositions.

EXAMPLE 1

PAP/PAOC Pre-treatment Experiment. Shampoo extraction

PAP = p-Aminophenol
PAOC = p-Amino-o-Cresol

Stock Solutions:
PAP=5wt% in milli-Q-water

PAOC=2wt% in Isopropanol
Hydrogen Peroxide (H₂O₂)=30wt%
Ammonium Hydroxide (NH₃)=30wt%

One-Step Conventional
Colouring pH 10-Ex 1A

0.4wt% PAP +
0.45wt% PAOC +
3.0wt% H₂O₂ +
2wt% NH₃ + milli-Q-water = 10ml total

<u>Ingredients</u>	<u>Levels wt%</u>	<u>pH</u>	<u>Colouring Time</u>
PAP	0.40%		
PAOC	0.45%		
H ₂ O ₂	3.00%		
NH ₃	2.00%		
Isopropanol	22.50%		
<u>Milli-Q-Water</u>	<u>71.65%</u>		
<u>Total</u>	<u>100.00%</u>	PH10	45min total

PAP/PAOC Pre-treatment Experiment. Shampoo extraction (cont'd)

Two-Step Colouring
Process - Sample2-Ex.1B

Step 1: 0.4wt% PAP +
0.45wt% PAOC
+ milli-Q-water = 5ml
total, 20min.

Ingredients	Levels wt%	pH	Colouring Time
Step 1			
PAP	0.40%		
PAOC	0.45%		
Isopropanol	22.50%		
Milli-Q-	26.65%		
Water			
Total for Step 1	50.00%	pH 7	20min

Step2

Step 2: 3wt% H₂O₂ +
2wt% NH₃ + milli-Q-
water = 5ml total,
25min.

H₂O₂ 3.00%

NH₃ 2.00%

Milli-Q- 45.00%

Water

Total for Step 2 50.00%

pH 10 25min

Methanol Extraction

20ml MeOH heated to 45C in glass container. 1g dyed hair tress
stirred 45C MeOH solution for 15min.

PAP/PAOC Pre-treatment Experiment. Shampoo extraction (cont'd)

Description of Samples	I.D.	After Dye			After MeOH Ext			Delta LAB values		
		L	A	B	L	A	B	L	A	B
PAP+PAOC+NH ₃ /H ₂ O ₂ conventional pH10. Dyed 45min (CONTROL)	C1	45.57	27.42	32.14	50.53	23.94	32.14	4.96	-3.48	0.00
SYSTEM A										
Step 1: PAP+PAOC pretreatment 20min	S2-1	44.97	29.78		46.81	26.97	32.55	1.84	-2.81	-1.14
Step 2: NH ₃ +H ₂ O ₂ dyed 25 min										
SYSTEM B										
Step 1: PAP+PAOC pretreatment with 1/2 amt NH ₃ 20min	S3-1	47.59	25.91	30.70	53	25.44	31.75	5.41	-0.47	1.05
Step 2: NH ₃ +H ₂ O ₂ dyed 25 min										
SYSTEM C										
Step 1: 1/2 amt PAP+PAOC pretreatment 20min	S4-1	46.78	26.91	31.16	49.98	23.94	31.06	3.20	-2.97	-0.10
Step 2: 1/2 amt PAP/PAOC + NH ₃ /H ₂ O ₂ dye 25 min										

PAP/PAOC Pre-treatment Experiment. Shampoo Extraction

PAP/PAOC

- 32 -

Colour Change/Colour Control:

Using L as a value of colour intensity in hair, it can be clearly observed that all 3 of the 2-step colour systems found in Example 1 had better colour retention compared to the conventional pre-mixed system.

EXAMPLE 2. : Two-Step Colouring Process.
Pre/post treatments at alkaline pH

Ingredients	Levels, wt. %	pH	Colouring time
Step 1			
p-Aminophenol	0.40		
	0.45		
4-Amino-3-hydroxytoluene	2.0	10	20 min
Ammonia (28%)	22.50		
Isopropanol	24.65		
Milli-Q-Water			
Step 1 Total	50		
Step 2			
Hydrogen Peroxide (30%)	3.00		
	2.00	10	25min
Ammonia (28%)	45.0		
Milli-Q-Water			
Step 2 Total	50		
Final Total	100		

- 33 -

Results: Hunter Lab values before extraction (after colouring) and after Shampoo and Methanol extractions

	L	a	b
Before Extraction	41.47	26.18	29.48
After Methanol Extraction	45.77	26.18	32.21
After Shampoo Extraction	43.01	25.44	29.79

5

EXAMPLE 3 : Two-Step Colouring Process. - Pre-treatment at neutral pH and post-treatment at alkaline pH

Ingredients	Levels, wt. %	pH	Colouring time
Step 1: p-Aminophenol 4-Amino-3-hydroxytoluene Isopropanol Milli-Q-Water	0.20 0.23 22.50 27.07	7	20 min
Step1 Total	50		
Step 2: p-Aminophenol 4-Amino-3-hydroxytoluene Hydrogen Peroxide (30%) Ammonia (28%) Milli-Q-Water	0.20 0.23 3.00 2.00 44.57	10.0	25min
Step2 Total	50		
Final Total	100		

10

- 34 -

Results: Hunter Lab values before extraction (after colouring) and after Shampoo and Methanol extractions

	L	a	b
Before Extraction	46.78	26.91	31.16
After Methanol Extraction	49.98	23.94	31.06
After Shampoo Extraction	48.02	20.52	28.06

5

ADDITIONAL EXAMPLES

EXAMPLE 4

10

Composition For The First Step:

	Ceteareth 23	3
	Cocoamidopropyl betaine	2
15	Cetyl alcohol	2.3
	Propylene glycol	2.5
	p-Amino-o-cresol	2.2
	Sodium hydroxide	1.0
	p-Phenylenediamine	1.0
20	Steareth 3	0.8
	EDTA	0.1
	p-Aminophenol	0.5
	Isoascrobic acid	0.1
	Sodium bisulfite	0.2
25	Fragrance	0.02
	Acetic acid	q.s pH 7.5
	Water	q.s. 100

30

- 35 -

Composition For The Second Step:

5 EXAMPLE 4 (Cont'd)

	Hydrogen peroxide	3.0
	Cetyl alcohol	2.0
	Ceteareth 23	0.5
10	Phosphoric acid	1.0
	Ammonia (28%)	q.s. pH 10
	Water	q.s. 100

15

The above compositions may be made by methods, which are known in the art.

A dual package, which can be employed in the products and kits of the present invention, is disclosed in U. S. Patent No. 6,082,588 to Markey et al, which is hereby incorporated by reference.

25 KIT CONTAINING AN INSTRUCTION SHEET

The invention also relates to a kit for carrying out the hair colouring method of the invention. The kit may comprise a hair colour developer solution, a hair colourant part and a post treatment solution, each in a separate container or in a dual container, as described herein. The kit also contains written instructions that explain how the compositions of the invention are used.

- 36 -

The consumer can admix the components of the kit according to written instructions, to obtain the aqueous reaction mixture. After treatment for a desired time the mixture of hair developer and hair dye may be removed,
5 preferably with water or a conventional shampoo or a conventional conditioning shampoo.

Alternatively, and with respect to an embodiment of the invention wherein hair dye precursors are in admixture with
10 the oxidizing compound, there is no need for the consumer to undertake a pre-mixing step, just prior to application to hair. The consumer contacts his or her hair with an admixture of hair dye precursors and the oxidizing compound and waits for about 5 minutes to about 60 minutes to elapse.
15 Then the consumer contacts his or her hair with the hair colour developer mixture which is the basifying composition, and allows about 5 minutes to about 6-0 minutes to elapse, and then the consumer rinses the hair.

20 Desired change in hair colour by the method of the invention is described by the mathematical formula described above. Desired change in hair colour can be achieved in a number of other ways. In the first instance, the consumer can initially compare his or her hair colour with desired
25 hair colour or the hair colour of a sample tress. Hair dyeing by the method of the invention can be repeated until his or her hair colour matches the desired hair colour.

Desired hair colour can also be reached by comparing
30 hair after each treatment until it matches hair tresses taken from the consumer during a prior treatment.

- 37 -

Desired hair colour can also be reached by testing the hair after each treatment with instruments, which measure the colour of the hair. When the measurements of hair colour of the treated hair reach a desired level, the treatment hair reach a desired level, the treatment can be stopped.

Indeed, reaching the desired hair colour can be achieved by the use of any matching or comparison method commonly employed in the art.

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention and all such modifications are intended to be included within the scope of the following claims.

- 38 -

CLAIMS:

1. A method for treating hair which comprises:
 - 5 a) contacting said hair with a substantially inactive mixture of oxidative hair dye precursors; and
 - b) allowing said mixture to remain in said hair for a period of about 30 seconds to about 60 minutes.
- 10 2. A method according to claim 1, which further comprises:
 - a) contacting said hair with a mixture of oxidizing compounds and a basifying compound;
 - 15 b) allowing said mixture to remain in said hair for a period of about 30 seconds to about 60 minutes.
3. A method according to claim 1, wherein said mixture of oxidative hair dye precursors comprises an oxidizing
20 compound and said mixture has about an acidic pH to about a neutral pH.
4. A method according to claim 3, which further comprises:
 - 25 a) contacting said hair with a basifying compound; and
 - b) allowing said basifying compound to remain in said hair for a period of about 30 seconds to about 60 minutes.

30

- 39 -

5. A method according to claim 1, wherein said mixture of oxidative hair dye precursors comprises a basifying compound.
- 5 6. A method according to claim 1, which further comprises:
- a) contacting said hair with an oxidizing compound for a period of about 30 seconds to about 60 minutes.
 - b) contacting said hair with a basifying composition;
10 and
 - c) allowing said basifying compound to remain in said hair for a period of about 30 seconds to about 60 minutes.
- 15 7. A method according to claim 1, wherein said mixture of oxidative dye precursors are selected from the group consisting of m-aminophenol; 3-methyl-p-aminophenol; 2,3-dimethyl-p-aminophenol; p-phenylene diamine; p-toluenediamine; p-phenylenediamine; 2-chloro-p-phenylenediamine; N-phenyl-p-phenylenediamine; N-2-methoxyethyl-p-phenylenediamine; N,N-bis-(hydroxyethyl)-p-phenylenediamine; 2-hydroxymethyl-p-phenylenediamine; 2-hydroxyethyl-p-phenylenediamine; 4, 4'-diaminodiphenylamine; 2,6-dimethyl-p-phenylenediamine; 2-isopropyl-p-phenylenediamine; N-(2-hydroxypropyl)-p-phenylenediamine; 2-propyl-p-phenylenediamine; 1,3-N, N-bis-(2-hydroxyethyl)-N, N-bis (4-aminophenyl)- 2-propanol; 2-methyl-4-dimethylaminoaniline; p-aminophenol; p- methylaminophenol; 3-methyl-p-aminophenol; 2-hydroxymethyl-p-aminophenol; 2-methyl-p-aminophenol; 2-(2-hydroxyethylaminomethyl)-p-aminophenol; 2-methoxymethyl-p-aminophenol; and 5-

- 40 -

aminosalicylic acid; catechol; pyrogallol; o-aminophenol; 2, 4-diaminophenol; 2,4,5-trihydroxytoluene; 1,2,4-trihydroxybenzene; 2-ethylamino-p-cresol; 2,3-dihydroxynaphthalene; 5-methyl-o-aminophenol; 6-methyl-o-aminophenol; and 2-amino-5-acetaminophenol; 2-methyl-1-naphthol; 1-acetoxy-2-methylnaphthalene; 1,7-dihydroxynaphthalene; resorcinol; 4-chlororesorcinol; 1-naphthol; 1,5-dihydroxynaphthalene; 2,7-dihydroxynaphthalene; 2-methylresorcinol; 1-hydroxy-6-aminonaphthalene-3-sulfonic acid; thymol (2-isopropyl-5-methylphenol); 1,5-dihydroxy-1,2,3,4-tetrahydronaphthalene; 2-chlororesorcinol; 2,3-dihydroxy-1,4-naphthoquinone; and 1-naphthol-4-sulfonic acid; m-phenylenediamine; 2-(2,4-diaminophenoxy)ethanol; N,N-bis(hydroxyethyl)-m-phenylenediamine; 2,6-diaminotoluene; N,N-bis(hydroxyethyl)-2,4-diaminophenetole; bis(2,4-diaminophenoxy)-1,3-propane; 1-hydroxyethyl-2,4-diaminobenzene; 2-amino-4-hydroxyethylaminoanisole; aminoethoxy-2,4-diaminobenzene; 2,4-diaminophenoxyacetic acid; 4,6-bis(hydroxyethoxy)-m-phenylenediamine; 2,4-diamino-5-methylphenetole; 2,4-diamino-5-hydroxyethoxytoluene; 2,4-dimethoxy-1,3-diaminobenzene; and 2,6-bis(hydroxyethylamino)toluene; m-aminophenol; 2-hydroxy-4-carbamoylmethylaminotoluene; m-carbamoylmethylaminophenol; 6-hydroxybenzomorpholine; 2-hydroxy-4-aminotoluene; 2-hydroxy-4-hydroxyethylaminotoluene; 4,6-dichloro-m-aminophenol; 2-methyl-m-aminophenol; 2-chloro-6-methyl-m-aminophenol; 2-hydroxyethoxy-5-aminophenol; 2-chloro-5-trifluoroethylaminophenol; 4-chloro-6-methyl-m-aminophenol; N-cyclopentyl-3-aminophenol; N-hydroxyethyl-4-methoxy-2-

- 41 -

methyl-m-aminophenol and 5-amino-4-methoxy-2-methylphenol;
2-dimethylamino-5-aminopyridine; 2,4,5,6-tetra-
aminopyrimidine; 4,5-diamino-1-methylpyrazole; 4,5-diamino-
1-hydroxymethyl pyrazole, 4,5-diamino-1-
5 hydroxyethylpyrazole; 1-phenyl-3-methyl-5-pyrazolone; 6-
methoxy-8-aminoquinoline; 2,6-dihydroxy-4-methylpyridine; 5-
hydroxy-1,4-benzodioxane; 3,4-methylenedioxyphenol; 4-
hydroxyethylamino-1,2-methylenedioxybenzene; 2,6-dihydroxy-
3,4- dimethylpyridine; 5-chloro-2,3-dihydroxypyridine; 3,5-
10 diamino-2,6- dimethoxypyridine; 2-hydroxyethylamino-6-
methoxy-3-aminopyridine; 3,4- methylenedioxyaniline; 2,6-
bis-hydroxyethoxy-3,5-diaminopyridine; 4- hydroxyindole; 3-
amino-5-hydroxy-2,6-dimethoxypyridine; 5,6-dihydroxyindole;
7-hydroxyindole; 5-hydroxyindole; 2-bromo-4,5-
15 methylenedioxyphenol; 6-hydroxyindole; 3-amino-2-
methylamino-6- methoxypyridine; 2-amino-3-hydroxypyridine;
2,6-diaminopyridine; 5-(3,5-diamino-2-pyridyloxy)-1,3-
dihydroxypentane; 3-(3,5-diamino-2-pyridyloxy)-2-
hydroxypropanol; 4-hydroxy-2,5,6-triaminopyrimidine, and
20 mixtures thereof.

8. A method according to claim 1 wherein said oxidation
hair dye precursor composition comprises:
- 25 a) about 0.001% to about 1.0% of an oxidation hair
dye precursor;
- b) about 0.001% to about 1.0% of a second oxidation
hair dye precursor; and
- c) an aqueous carrier.

- 42 -

9. A method according to claim 1 wherein said oxidation hair dye precursor composition comprises:
- a) about 0.02% to about 0.1% of an oxidation hair dye precursor;
 - 5 b) optionally about 0.02% to about 0.1% of a second oxidation hair dye precursor; and
 - c) an aqueous carrier.
- 10 10. A method according to claim 5 wherein said oxidation hair dye precursor composition comprises:
- a) about 0.01 to about 10% of an oxidative compound;
 - b) about 0.01 to about 5% of a basifying compound;
 - 15 and
 - c) an aqueous carrier.
11. A method according to claim 1 wherein said oxidative composition comprises
- 20 a) about 0.1 to about 5.0% of an oxidative compound;
 - b) about 0.1 to about 3.0% of a basifying agent; and
 - 25 c) an aqueous carrier.

- 43 -

12. A method according to claim 3 wherein said mixture of oxidative hair dye precursors comprises:
- 5 a) about 0.001% to about 5.0% of an oxidation hair dye precursor;
 - b) about 0.001% to about 3.0% of a second oxidation hair dye precursor;
 - c) about 0.1 to about 4.5% of an oxidative compound; and
 - 10 d) an aqueous carrier.
13. A method according to claim 12 wherein said mixture of oxidative hair dye precursors comprises
- 15 a) about 0.1% to about 3.0% of an oxidation hair dye precursors;
 - b) about 0.1% to about 3.0% of a second oxidation hair dye precursor;
 - c) about 0.1 to about 4.0% of an oxidative compound; and
 - 20 d) an aqueous carrier.
14. A method according to claim 1, wherein said mixture of oxidative hair dye precursors comprising a basifying compound comprises:
- 25 a) about 0.1 to about 1% of an oxidative compound;
 - b) about 0.1 to about 3.0% of a second oxidation hair dye precursor;
 - 30 a) about 0.1 to about 1.5% of a basifying compound; and

- 44 -

b) an aqueous carrier.

15. A method according to claim 2 wherein said oxidative compound is selected from the group consisting of
5 hydrogen peroxide, urea peroxide, melamine peroxide, sodium perborate and sodium percarbonate.
16. A method according to claim 1, for treating hair which comprises providing said hair longer lasting colour.
- 10 17. A kit for permanently colouring hair which comprises:
- a) a hair colourant composition in a container,
b) a hair developer composition in a container, and
15 c) written instructions that direct that the hair colourant part is applied to the hair as a substantially inactive mixture for about 30 seconds to about 60 minutes.
18. A method according to claim 1, wherein the rate of
20 oxidation of hair dye precursors/rate of diffusion of hair dye precursors ≤ 1 .

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 August 2003 (21.08.2003)

PCT

(10) International Publication Number
WO 03/068177 A3

(51) International Patent Classification⁷: **A61K 7/13**

River Road, Edgewater, NJ 07020 (US). **CHAN, Alexander, Chung, Bong**; Unilever R & D Edgewater, 45 River Road, Edgewater, NJ 07020 (US).

(21) International Application Number: **PCT/EP03/01400**

(22) International Filing Date: 12 February 2003 (12.02.2003)

(74) Agents: **TANSLEY, Sally, Elizabeth et al.**; Unilever PLC, Patent Department, Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/075,745 14 February 2002 (14.02.2002) US

(81) Designated States (*national*): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK (utility model), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(71) Applicant (*for AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, OM, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only*): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SN, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only*): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

Published:

— with international search report

(71) Applicant (*for IN only*): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, 400 020 Mumbai (IN).

(88) Date of publication of the international search report:
24 December 2003

(72) Inventors: **SAROJINI, Padmaja**; Unilever R & D Edgewater, 45 River Road, Edgewater, NJ 07020 (US). **BAR-TOLONE, John, Brian**; Unilever R & D Edgewater, 45

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/068177 A3

(54) Title: TWO STEP PERMANENT COLOURING OF HAIR

(57) Abstract: A method for treating hair which comprises: first contacting said hair with a substantially inactive mixture of oxidative hair dye precursors; and allowing said mixture to remain in said hair for a period of about 30 seconds to about 60 minutes; followed by contacting said hair with a developer to achieve long lasting hair colour change, is described.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/01400

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/13

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 823 503 A (MONSAVON-L'ORÉAL) 11 November 1959 (1959-11-11) claims 1-12; example I ---	1,2,7,9, 15,16
X	US 4 314 810 A (C. FOURCADIER ET AL.) 9 February 1982 (1982-02-09) claims 18-27; examples 3,5,9,10 ---	1,2,5, 7-11, 14-16
X	EP 0 827 739 A (L'ORÉAL) 11 March 1998 (1998-03-11) page 7, line 38 - line 41; claims 1-29; example 1 ---	1,3-5, 7-17
A	EP 0 722 711 A (L'ORÉAL) 24 July 1996 (1996-07-24) claims 1-12; examples 2,3 ---	1-18
-/-		

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

15 August 2003

Date of mailing of the international search report

26/08/2003

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Willekens, G

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/01400

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 826 669 A (L'ORÉAL) 4 March 1998 (1998-03-04) claims 1-16; examples 1,2 -----	1-18

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/01400

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 823503	A	11-11-1959	BE 564450 A	
			CH 347814 A	31-07-1960
			DE 1097086 B	12-01-1961
			FR 1166172 A	04-11-1958
			NL 107681 C	
			NL 224577 A	
			US 2934396 A	26-04-1960
US 4314810	A	09-02-1982	FR 2431860 A1	22-02-1980
			BE 877917 A1	28-01-1980
			CA 1144863 A1	19-04-1983
			CH 641953 A5	30-03-1984
			DE 2930358 A1	07-02-1980
			GB 2026553 A ,B	06-02-1980
			IT 1123492 B	30-04-1986
			JP 1516593 C	07-09-1989
			JP 55020784 A	14-02-1980
			JP 63064401 B	12-12-1988
EP 827739	A	11-03-1998	FR 2753093 A1	13-03-1998
			AT 182779 T	15-08-1999
			AU 688246 B1	05-03-1998
			BR 9702829 A	29-12-1998
			CA 2214021 A1	06-03-1998
			CN 1186655 A ,B	08-07-1998
			DE 69700376 D1	09-09-1999
			DE 69700376 T2	25-11-1999
			EP 0827739 A1	11-03-1998
			ES 2138853 T3	16-01-2000
			HU 9701480 A1	28-08-1998
			JP 3024088 B2	21-03-2000
			JP 10101538 A	21-04-1998
			KR 264926 B1	01-09-2000
			PL 321949 A1	16-03-1998
			RU 2158583 C2	10-11-2000
			US 6074439 A	13-06-2000
			US 6527814 B1	04-03-2003
			US 5976195 A	02-11-1999
EP 722711	A	24-07-1996	FR 2729567 A1	26-07-1996
			AT 148987 T	15-03-1997
			AU 678921 B2	12-06-1997
			AU 4094296 A	01-08-1996
			BR 9600460 A	03-03-1998
			CA 2167647 A1	21-07-1996
			CN 1138454 A	25-12-1996
			DE 69600003 D1	27-03-1997
			DE 69600003 T2	05-06-1997
			EP 0722711 A1	24-07-1996
			ES 2100769 T3	16-06-1997
			HU 9600112 A1	30-12-1996
			JP 2880112 B2	05-04-1999
			JP 8231357 A	10-09-1996
			PL 312398 A1	22-07-1996
			US 5804171 A	08-09-1998
EP 826669	A	04-03-1998	FR 2752575 A1	27-02-1998
			DE 69700299 D1	05-08-1999

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/01400

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 826669	A	DE 69700299 T2	04-11-1999
		EP 0826669 A1	04-03-1998
		ES 2135973 T3	01-11-1999
		JP 2991681 B2	20-12-1999
		JP 10087449 A	07-04-1998
		US 5876465 A	02-03-1999